Evaluation of Historical Beryllium Abundance in Soils, Airborne Particulates and Facilities at Lawrence Livermore National Laboratory

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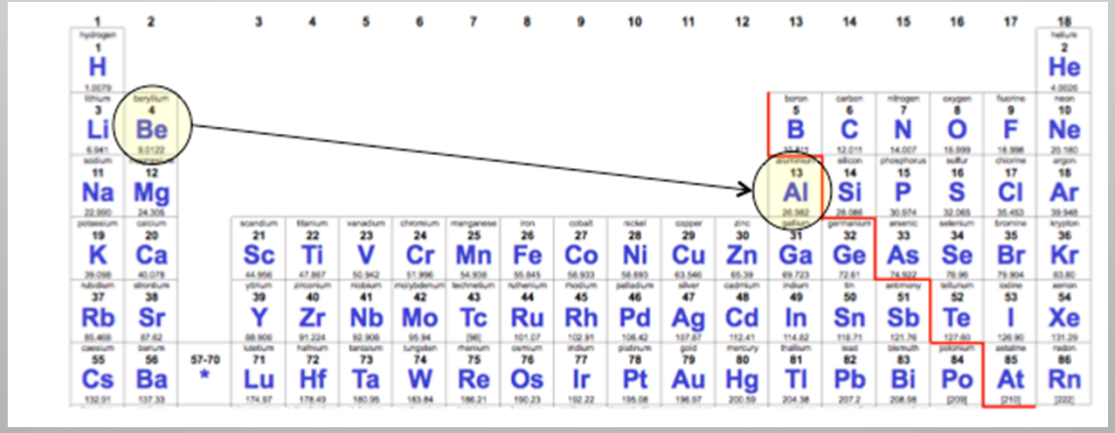
Beryllium Geochemistry

- A naturally occurring element found in soil, rocks, groundwater and atmospheric dust

- Resides in Group II of the periodic table, but chemistry similar to Al (III), exhibiting a “diagonal relationship” due to small ionic radius



Beryllium Contamination

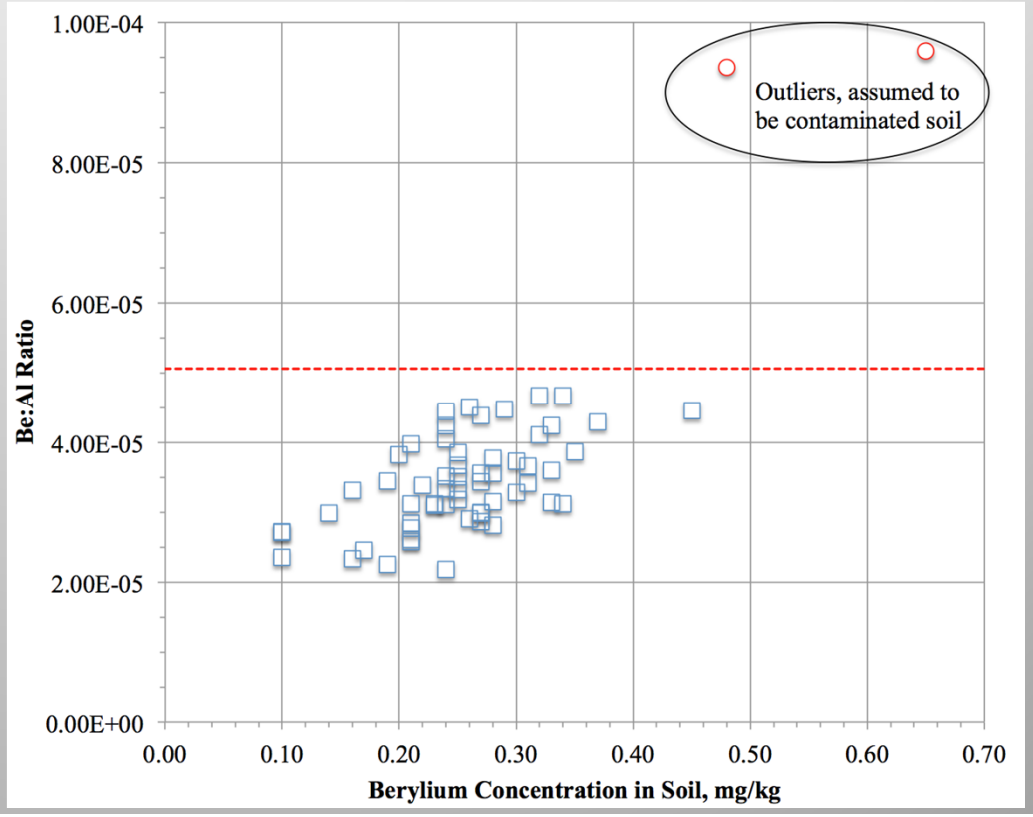
- Identified at 73 US Department of Defense (DOD) facilities (USGAO, 2001),
- At over 300 Department of Energy (DOE) related sites including contractors (USDOE, 2010; USGAO, 2001),
- OSHA identified hundreds of beryllium-use sites across the US (USGAO, 2001)

Beryllium Surface Contamination

- 10 CFR 850 release criteria for surface contamination is 0.2 µg/100cm^2
- Furthermore, 10 CRF 850 sets release rates for bulk samples at “the concentration level of beryllium in local soil at the point of release”
- Bulk samples are commonly taken when assessing soil or facility contamination
  - This presents a problem, especially where natural beryllium levels in soils are high, or where Be is present as an impurity rather than a commodity.

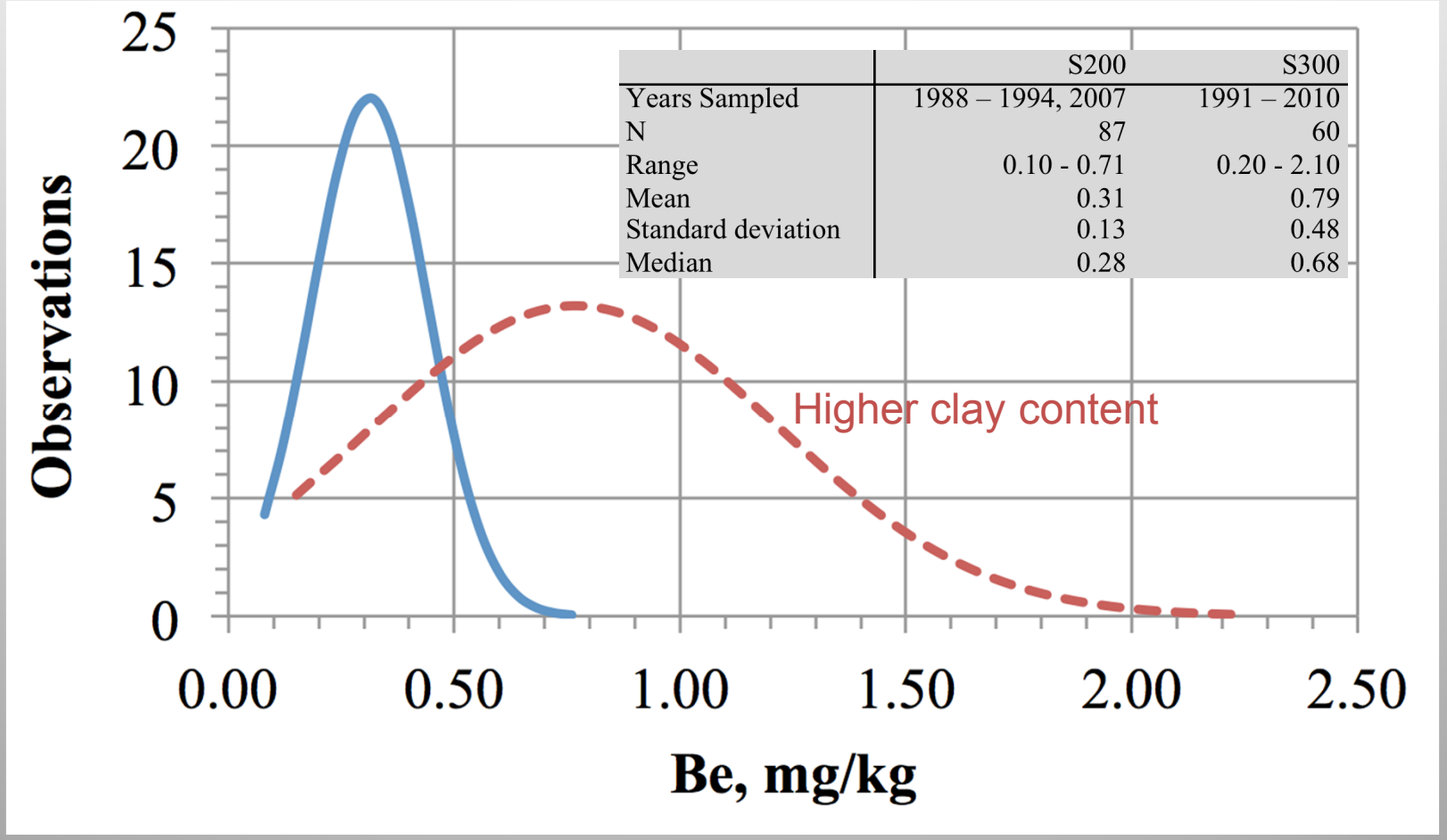
LLNL S200 Soil Be:Al Study (2007)

Beryllium and aluminum concentrations for 60 S200 soil samples analyzed in 2007 (Mullins and Kamerzell, red circles considered outliers using a $UTL_{95\%,95\%}$ = 5.07 x10^{-5} red dashed line)



LLNL Soils 1988-2010

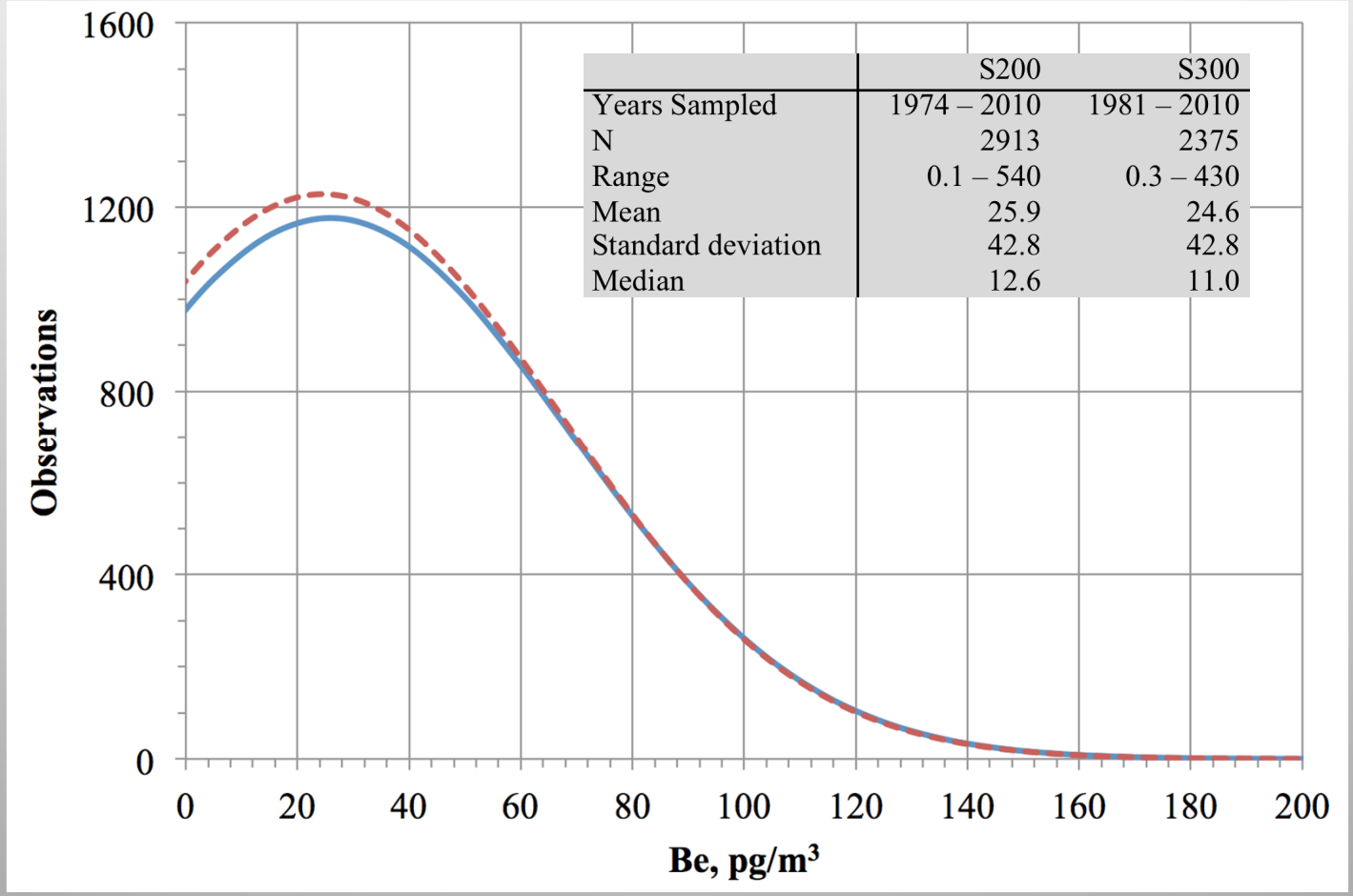
Main site (S200) and annex site (S300)



	S200	S300
Years Sampled	1988 – 1994, 2007	1991 – 2010
N	87	60
Range	0.10 - 0.71	0.20 - 2.10
Mean	0.31	0.79
Standard deviation	0.13	0.48
Median	0.28	0.68

LLNL Air Particulates 1974-2010

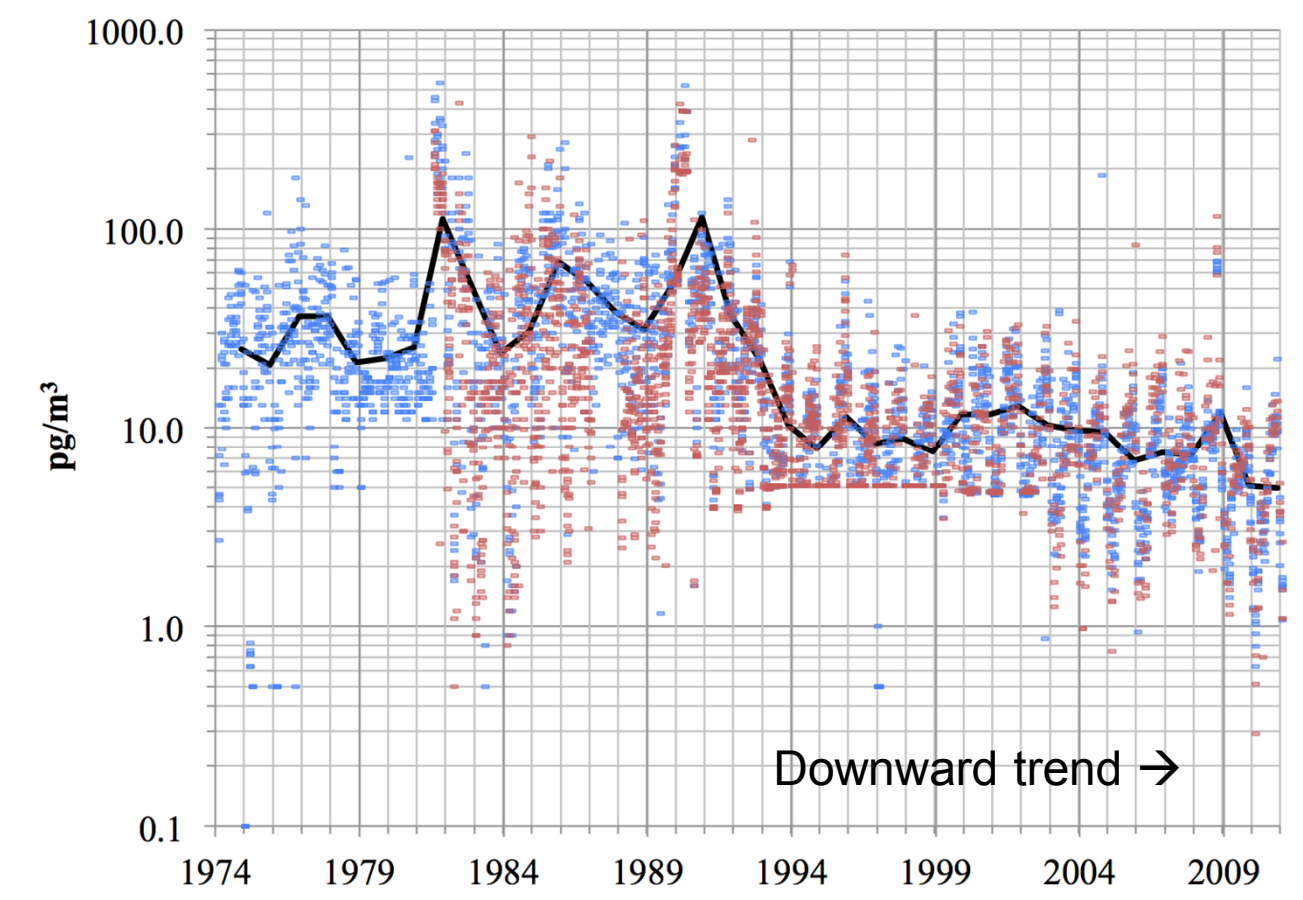
Main site (S200) and annex site (S300)



	S200	S300
Years Sampled	1974 – 2010	1981 – 2010
N	2913	2375
Range	0.1 – 540	0.3 – 430
Mean	25.9	24.6
Standard deviation	42.8	42.8
Median	12.6	11.0

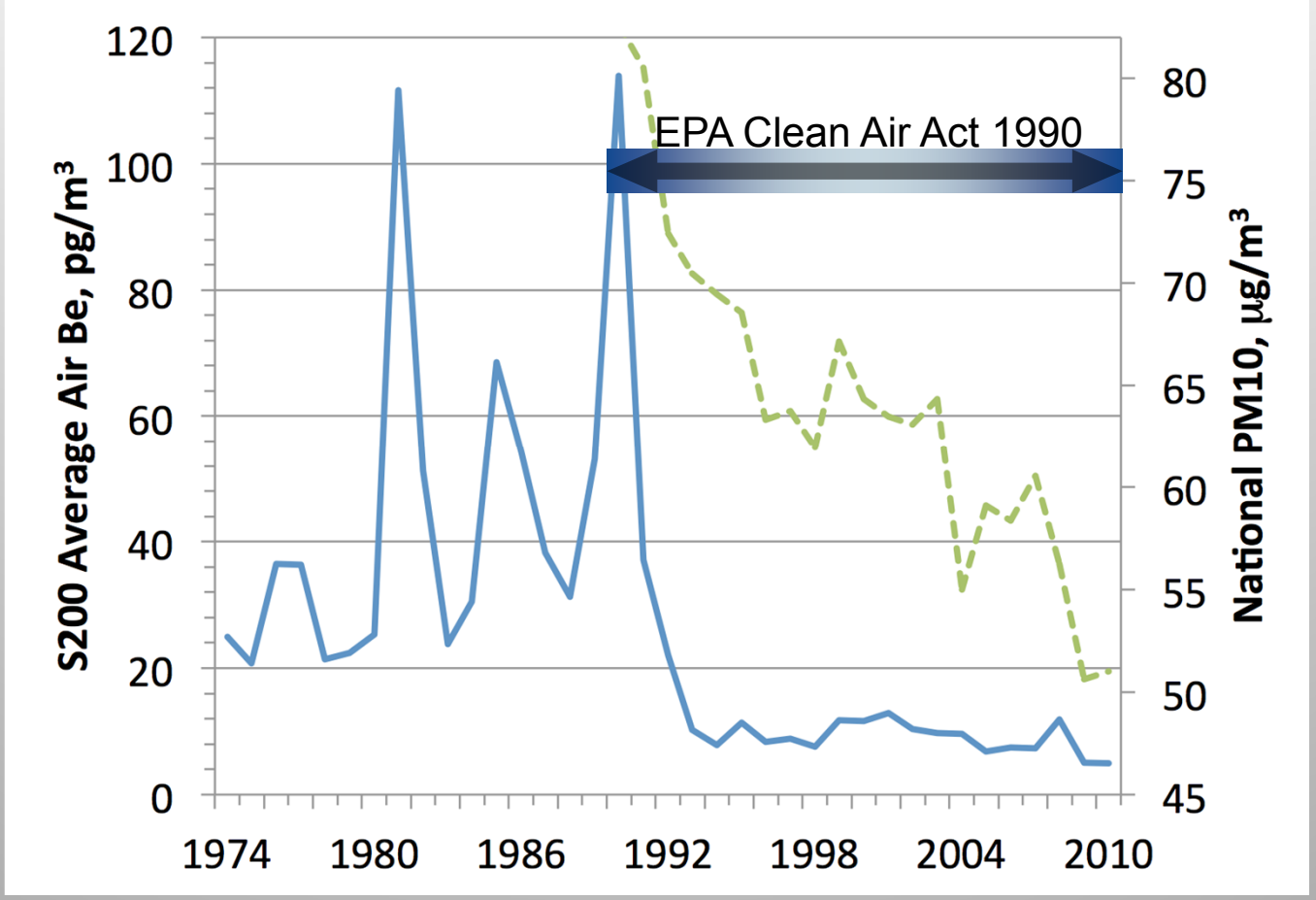
LLNL Monthly Air Samples 1974-2010

Main site (S200), annex site (S300) and annual average



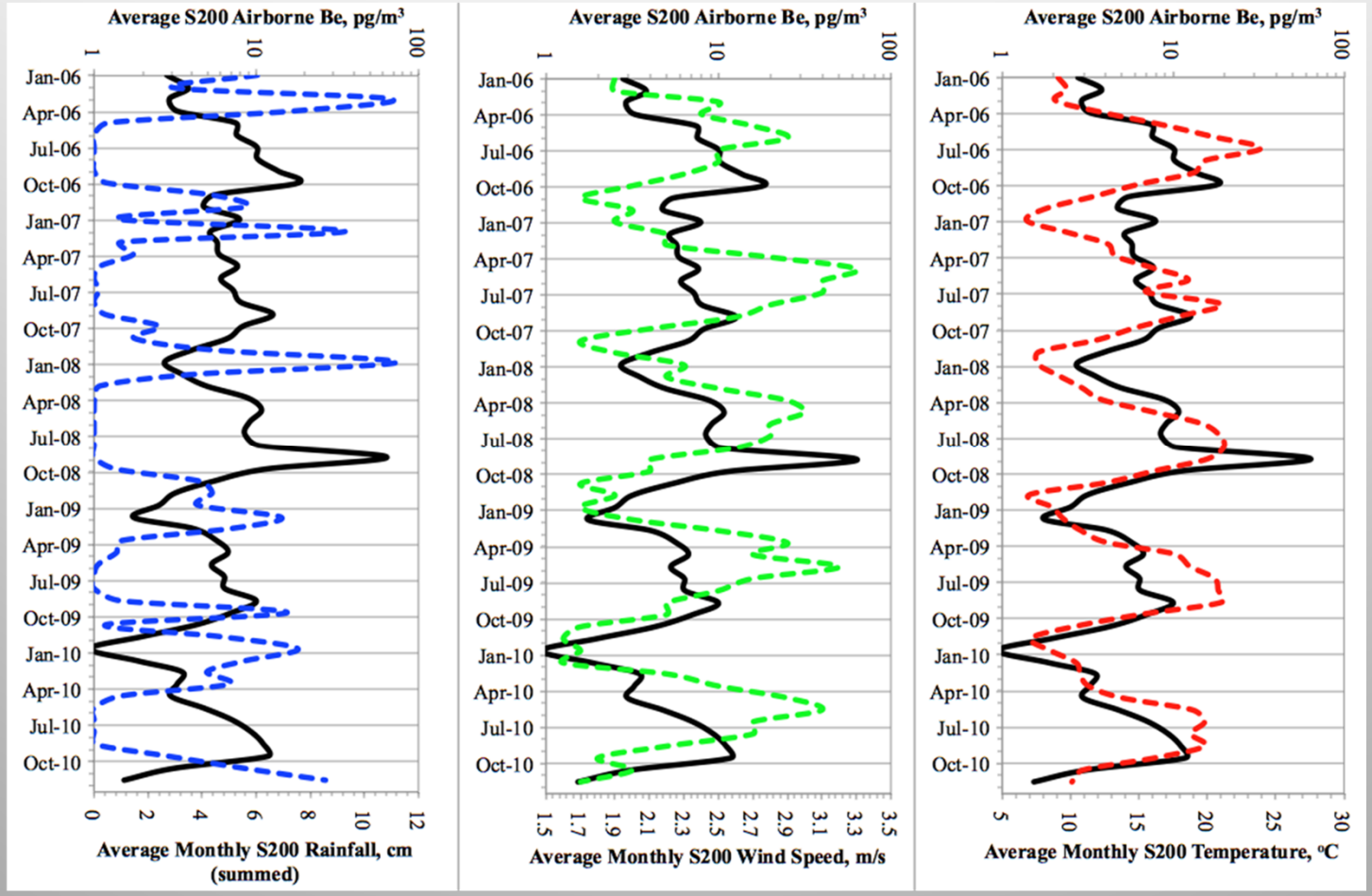
LLNL Annual Air Samples 1974-2010

LLNL air samples and national PM10 data (EPA 2012)



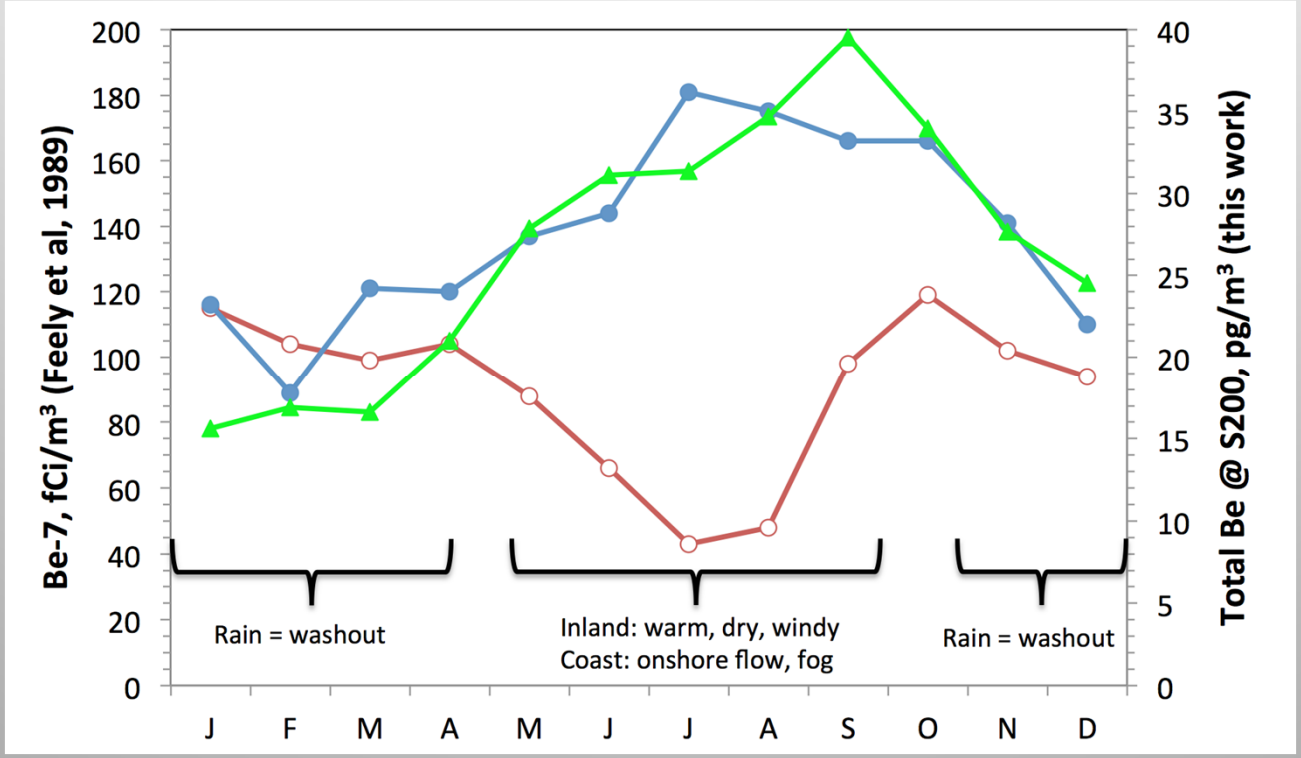
Seasonal Periodicity in Air Samples

Peaks observed in summer, troughs in winter, all years.



Seasonal Periodicity in Air Samples

Measured Be (LLNL 1973 to 1980), overlaid on local Be-7 (Feely et al 1989) measurements (Richmond, CA 1973 to 1977 and Tracy, CA 1977 to 1981)

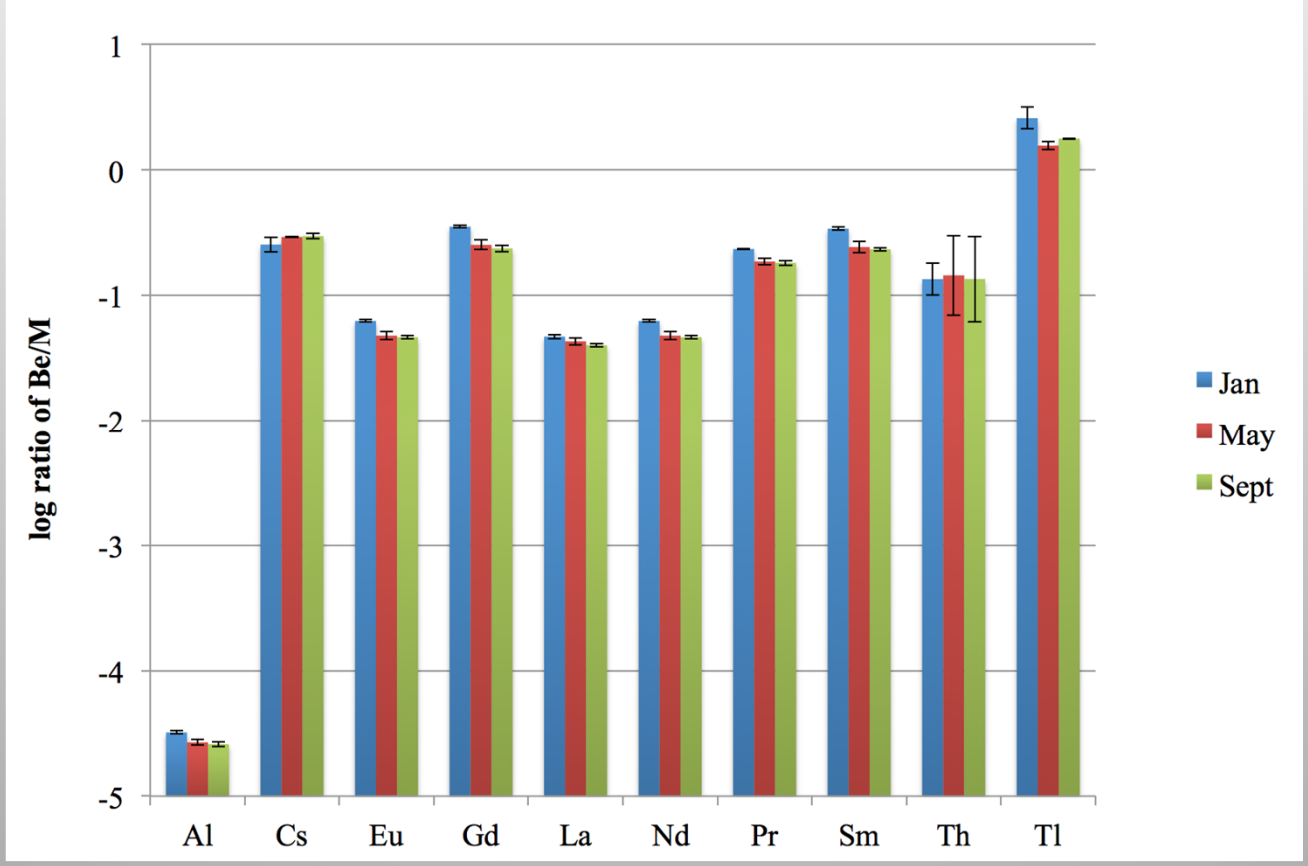


Multi-Element Analysis

- The composition of airborne particulates is typically driven by soil resuspension and industrial processes
- It is reasonable to assume that soil, air and surfaces that are contaminated with man-made beryllium would have elevated beryllium concentrations in relation to these analogous elements
- By evaluating the ratio of beryllium to other elements in soil and outside air, it is possible to compare natural beryllium with process-induced beryllium from facilities
- Using clean LLNL soils we identified good correlation between Be and Al, Cs, Eu, Gd, La, Nd, Pr, Sm, Th, Tl

Multi-Element Analysis of Periodicity

Winter, spring and summer ratios of Be/M in airborne particulates collected at LLNL during 2008



Analysis of Facility Carpet Dirt

- Bulk environmental sampling was conducted to investigate the presence and relative level of beryllium entrained in carpets within LLNL facilities (Sutton 2009)
- Vacuuming found Be between 0.002 to 0.480 µg/100 cm^2 (mean: 0.080, median: 0.053, SD: 0.086 µg/100 cm^2)
- Compare to the DOE release criterion of 0.2 µg/100 cm^2
- In some cases, the beryllium in carpet > RC wrt mass per unit area. However, the RC does not explicitly consider carpet cleanliness (e.g. dirt loading, dirt composition, age, foot traffic, proximity to exterior door/window, cleaning frequency) → multi-element analysis

Multi-Element Analysis Facility Dust

			Facility ID								
			A	**B**	**C**	**D**	**E**	**F**	**G**	**H-1**	**H-2**
Known Be activity[a] / equipment[b]			No	No	No	Yes[a]	Yes[a]	Yes[a]	No	Yes[b]	Yes[b]
Be:M Ratio	**LLNL Soil**	**LLNL Air**									
Al (10^{-5})	2.04	3.76	2.91	2.31	*16.0*	*187*	*17.4*	*78.9*	1.55	1.86	*6.82*
Cs	0.566	0.365	*0.481*	0.118	0.272	*0.707*	0.333	*4.19*	*1.13*	0.227	*0.710*
Eu	1.33	1.81	1.09	1.38	*8.00*	*37.6*	*8.29*	*17.0*	*2.67*	0.659	*2.35*
Gd	0.252	0.445	0.218	0.206	*1.50*	*11.0*	*1.81*	*3.75*	0.246	0.153	0.414
La (10^{-2})	6.93	5.34	3.74	3.60	*16.0*	*314*	*17.2*	*106*	5.26	3.15	*7.64*
Nd (10^{-2})	7.43	7.56	4.51	3.92	*31.8*	*445*	*34.0*	*49.2*	*10.4*	3.77	*10.3*
Pr	0.293	0.277	0.174	0.156	*1.11*	*17.9*	*1.18*	*2.03*	*0.449*	0.143	*0.361*
Sm	0.393	0.427	0.266	0.125	*1.70*	*18.3*	*1.65*	*8.04*	*0.615*	0.207	*0.690*
Th	0.213	0.157	*0.169*	0.128	*1.51*	*23.0*	*1.63*	*3.32*	*0.404*	0.139	*0.443*
Tl	3.33	3.58	*5.00*	*6.56*	*11.7*	*589*	*13.6*	*29.0*	*9.64*	2.90	*10.0*
	Number > LLNL Soil		2	3	9	10	9	10	7	0	10
	Number > LLNL Air		3	1	9	10	9	10	7	0	9

Conclusions

- Review of LLNL 2007 study identified 2 areas of localized contaminated soil
- Mean S200 soil contains 0.31 mg/kg with S300 higher due to higher smectite content
- Mean LLNL air particles contain ~25 pg/m^3 Be, well below historic levels and requirements
- Downward trend in atmospheric Be likely due to EPA CAA implementation in U.S.
- Periodicity each year with seasons due to local meteorological phenomena

Conclusions

- Multi-element analysis of archived air filter samples showed no significant increase in the Be:M ratio during Jan, May, Sept months in 2008
  - Suggests that periodicity in beryllium levels not related to LLNL activities
- Multi-element analysis was used to evaluate carpet dirt samples allowing distinction between contaminated facilities, clean facilities and tracked beryllium
- This work established new background Be levels for LLNL and provides guidance on how other beryllium-handling facilities should proceed in determining background levels with regard to release criteria

More information

More information on this study can be found in:

- Sutton et al. (2012) *Evaluation of historical beryllium abundance in soils, airborne particles and facilities at Lawrence Livermore National Laboratory,* Published in Science of the Total Environment 437:373-383

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HIGHLIGHTS

- We examined beryllium concentrations in historical on-site soil samples and local air particulates.
- We evaluated beryllium-to-metal ratios for soil and air filter samples and applied results to samples from facility carpets.
- Localized areas of contamination were identified, but operations do not appear to have increased Be in local air and water.
- Variation in airborne beryllium correlates to local weather patterns and PM10 levels and not to operational activities.
- Multi-element analysis provided information to determine whether the source of Be was natural or anthropogenic.

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ABSTRACT

Beryllium has been historically machined, handled and stored in facilities at Lawrence Livermore National Laboratory (LLNL) since the 1950s. Additionally, outdoor testing of beryllium-containing components has been performed at LLNL's Site 300 facility. Beryllium levels in local soils and atmospheric particulates have been measured over three decades and are comparable to those found elsewhere in the natural environment. While localized areas of beryllium contamination have been identified, laboratory operations do not appear to have increased the concentration of beryllium in local air or water. Variation in airborne beryllium correlates to local weather patterns, PM10 levels, normal sources (such as resuspension of soil and emissions from coal power stations) but not to LLNL activities. Regional and national atmospheric beryllium levels have decreased since the implementation of the EPA's 1990 Clean-Air-Act. Multi-element analysis of local soil and air samples allowed for the determination of comparative ratios for beryllium with over 50 other metals to distinguish between natural beryllium and process-induced contamination. Ten comparative elemental markers (Al, Cs, Eu, Gd, La, Nd, Pr, Sm, Th and Ti) that were selected to ensure background variations in other metals did not collectively interfere with the determination of beryllium sources in work-place samples at LLNL. Multi-element analysis and comparative evaluation are recommended for all workplace and environmental samples suspected of beryllium contamination. The multi-element analyses of soils and surface dusts were helpful in differentiating between beryllium of environmental origin and beryllium from laboratory operations. Some surfaces can act as "sinks" for particulate matter, including carpet, which retains entrained insoluble material even after liquid based cleaning. At LLNL, most facility carpets had beryllium concentrations at or below the upper tolerance limit determined by sampling facilities with no history of beryllium work. Some facility carpets had beryllium concentrations above the upper tolerance limits but can be attributed to tracking of local soils, while other facilities showed process-induced contamination from adjacent operations. In selected cases, distinctions were made as to the source of beryllium in carpets. Guidance on the determination of facility beryllium sources is given.

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